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Thermal runaway risk evaluation of Li-ion cells using a pinch–torsion test

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HIGHLIGHTS

- A pinch–torsion test is designed to evaluate Li-ion cell safety under simulated internal short-circuit conditions.
- The torsion component can trigger internal short-circuit at a lower load with smaller short spot size.
- TRR (thermal runaway risk) scores are proposed to rate cell safety performance.
- This method can distinguish commercial cell safety performance in a wide range of state of charge.

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ABSTRACT

Internal short circuit (ISCr) can lead to failure of Li-ion cells and sometimes result in thermal runaway. Understanding the behavior of Li-ion cells in ISCr condition is thus critical to evaluate the safety of these energy storage devices. In the current work, a pinch–torsion test is developed to simulate ISCr in a controlled manner. It is demonstrated that the torsional component superimposed on compression loading can reduce the axial load required to induce ISCr with smaller short spot size. Using this pinch–torsion test, two types of commercial Li-ion pouch cells were tested under different state of charge (SOC). Based on the severity of the cell damage, a series of thermal runaway risk scores were used to rate the thermal stability of these cells. One of the cell types showed significantly increased hazard as the SOC increased while the other type exhibited relative uniform behavior among different SOC. Therefore, this novel pinch–torsion test seems to be an attractive candidate for safety testing of Li-ion cells due to its abilities to consistently create small ISCr spots and to differentiate cell stability in a wide range of SOC.

1. Introduction

In recent years, safety issues of Li-ion batteries have received much attention due to their increased applications in consumer electronics, transportation, and power grid energy storage. Internal short circuit (ISCr), which can occur due to manufacturing imperfection, operational abuse, or mechanical abuse, is believed to be a major cause of field incidents associated with commercial Li-ion batteries [1,2]. If a large amount of energy is released during ISCr, local temperature rise could trigger various chemical reactions [3], which may lead to thermal runaway and in some extreme cases fires and explosions [4].

Various testing methods have been developed to simulate the ISCr events, including forced ISCr test [5], nail penetration [5–7], small indentation [7,8], and cell pinch test [1]. While these methods face difficulties in introducing small, isolated ISCr spots in a reproducible manner, an improved pinch test developed by Cai et al. [2] demonstrated good repeatability in creating ISCr with controllable size in Li-ion and Li-ion–polymer cells. The size of the ISCr spots was varied by changing the stroke-return voltage; and ISCr spots as small as 1–2 mm were easily reproduced [2].

However, this test experienced difficulties in testing cells with a high state of charge (SOC). For example, when comparing three different cell types, 100% of each type went thermal runaway at a charged voltage of 4.2 V [2], making it impossible to distinguish the thermal stability of these cells. Similar results were observed when applying this pinch test to large-capacity cells (15–25 A h) during which thermal runaway was often encountered. After careful examination of puncture locations in the failed cells, it was believed the areas experiencing higher percentage of tension failed much earlier than areas under compression. In order to demonstrate this observation a simple anode/separator/cathode sandwich structure was tested on an MTS machine that can apply a “twist” in the X–Y

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plane during compressive loading in the Z-direction. When a small rotation was applied during the compression, the separator failed at a smaller loading force. When the same tests were repeated on small pouch cells, ISCr could be induced (as indicated by a voltage drop) without causing severe thermal runaway. These preliminary results suggested that a combined pinch and X–Y torsion could generate smaller ISCr spot size than the pinch only.

Although it is hard to confirm after a field thermal runaway event, it is believed that the actual spot size of ISCr is usually very small. Possible sources for ISCr are Li dendrites formed during cell operation and machining debris/metal particles introduced in the manufacturing process. Therefore, generating smaller ISCr size can better simulate the field conditions. Furthermore, reducing the short size could induce ISCr without causing catastrophic damage, making it possible to distinguish safety behavior under high SOC.

The hypothesis that torsion can reduce the ISCr size during pinch test was demonstrated through two series of experiments. Comparison between the pinch-only and pinch–torsion tests was first performed on a three-layer (anode-separator-cathode) dry cell mentioned above, and then extended to multi-layer Li-ion pouch cells. Using the new pinch–torsion test, two types of commercial Li-ion pouch cells were then examined. These cells exhibited different thermal responses under various SOCs. The combined pinch–torsion tests were able to distinguish ISCr behaviors of fully charged (4.2 V) Li-ion cells. A thermal runaway risk (TRR) scoring system was also proposed to evaluate the thermal stability of Li-ion cells based on the changes of cell temperature and voltage under ISCr testing.

2. Experimental method

Pinch–torsion tests were performed on a commercial axial/torsional servo-hydraulic testing machine (Model 809, MTS, Eden Prairie, MN, USA). Two steel loading rods were aligned to pinch the Li-ion cells from both directions. The ends of the loading rods were hemispheres with a diameter of 12.7 mm. The test set-up is shown in Fig. 1a. Displacement control was used in all tests.

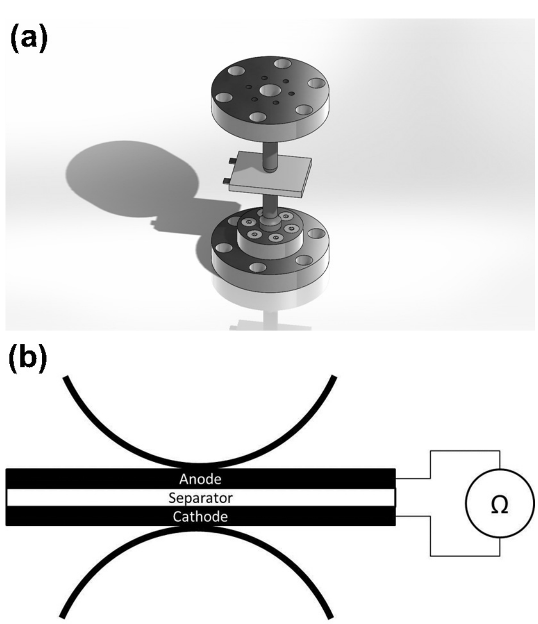

Fig. 1. Schematics showing the (a) pinch–torsion test setup and (b) the three-layer dry cell configuration.

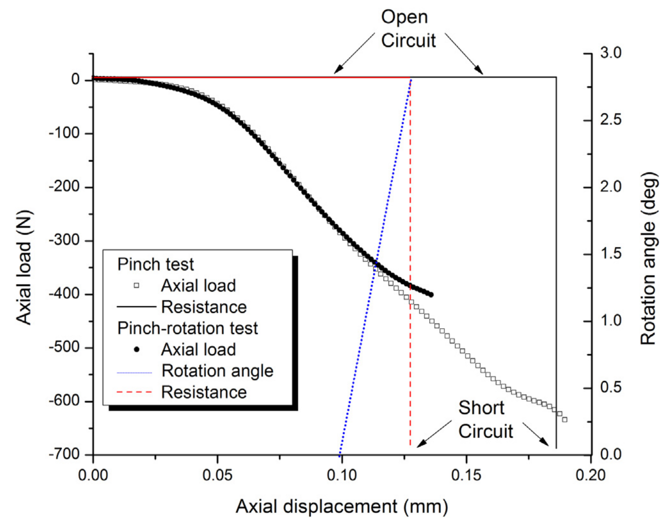

Fig. 2. Comparison of loading curves during pinch and pinch–torsion tests of the prototype cells. The abscissa shows the movement of the testing rod in the direction parallel to the cell thickness (the axial direction). The ordinate on the left hand side shows the force in the axial direction and the ordinate on the right hand side shows the measured angle of rotation (pinch torsion test only).

For the prototype dry cells, the resistance between the positive and the negative electrodes was monitored. When ISCr occurs, this resistance would change from infinity (open circuit) to a definite value (typically a fraction of Ohm). For the pouch cells, the voltage between the positive and negative electrodes was monitored. The occurrence of ISCr was determined when a voltage drop of 0.1 V was detected [2]. Temperature on the outside surface of the cells was recorded using thin film thermocouples. For commercial Li-ion cells testing, an enclosure box connected to the exhaust and filtering systems was used.

While the original pinch test can be applied to pouch cells and prismatic cells in aluminum cans, the pinch–torsion test only applies to pouch cells since our preliminary results suggested additional torsion did not prompt earlier failure when testing the latter. It is because the effective torsion force depends on not only the normal compressive force but also the friction between the contact surfaces. It was likely that the friction between the steel loading rods and the aluminum can was too small to be effective in transferring the torsion force.

After testing, cells were opened and damaged separators were examined using optical microscopy.

3. Pinch test versus pinch–torsion test

This section will discuss pinch-only and pinch–torsion tests performed on the dry cells as well as multi-layered pouch cells.

3.1. Prototype cells

To explore the effect of torsional component on creating ISCr during pinch tests, dry cells (Fig. 1b) were constructed from common materials used in commercial Li-ion batteries. A graphitic anode layer, a polymeric separator, and an LCO-coated aluminum cathode layer were stacked and encapsulated without electrolyte using polymeric pouch material. Metal tabs were attached to the electrodes for the measurement of electrical resistance. The lateral size of the dry cells was approximately 50 mm × 80 mm. Since no electrolyte was used, the electrical resistance between the anode and the cathode was monitored and used to determine the occurrence of ISCr (Fig. 1b). The axial loading rate in pinch-only and

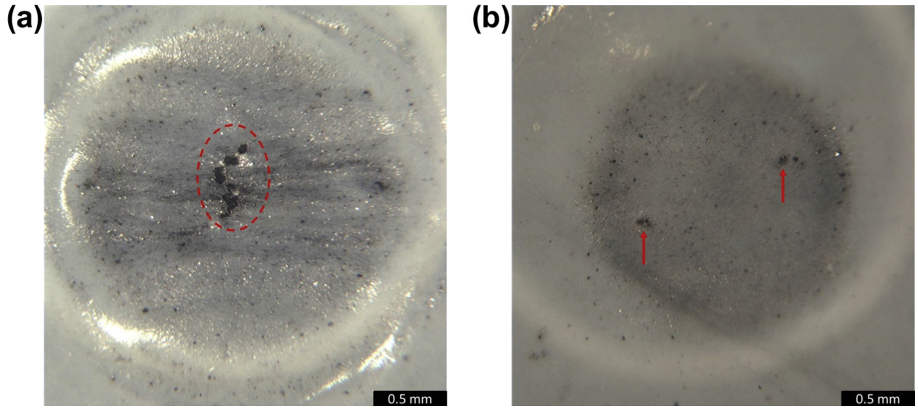

Fig. 3. Pictures showing the damaged separators after (a) pinch test, and (b) pinch–torsion test. The circular deformed regions appeared darker because they were thinner and the sample stage was black. Circle and arrows indicate holes in the separators.

pinch–torsion tests was fixed at 0.01 mm s^{-1}. During the pinch–torsion tests, a small rotation was applied after the axial load reached 310 N, which was approximately 50% of the failure load determined from the pinch-only tests.

The effect of torsion on ISCr is clearly illustrated in Fig. 2. For both pinch and pinch–torsion tests, the loading curve showed very similar trends: the axial load increased relatively slowly in the beginning and then became relatively linear (Fig. 2). In the pinch–torsion test, when the torsion was introduced at 310 N, the loading curve deviated from the linear region and electrical short (as indicated by the sudden drop of resistance) occurred after ~2.7° of rotation at approximately 400 N of axial load, which is 36.5% lower than the failure load observed in the pinch-only test (630 N).

After testing, separator layers were examined for damage. As expected all separators had circular deformed zones where the plastic film became semi-clear due to thinning, while the rest remained opaque. Under pinch-only test conditions, typical damage in the separator consisted of a series of small holes ~0.1 mm in diameter located near the central region of the deformed zone (Fig. 3a). When torsion was added, the deformed regions became smaller, and the hole size was reduced to approximately 0.05 mm in diameter (Fig. 3b). The smaller damage size generated by the pinch–torsion test corresponded to the lower load required to induce ISCr, both of which implied that a small amount of rotational movement would trigger ISCr at an earlier stage in this type of pinch test.

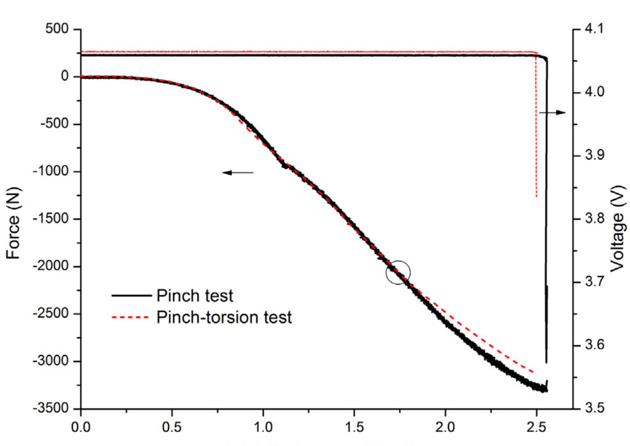

Fig. 4. Comparison of loading curves during pinch and pinch–torsion tests of Li-ion pouch cells.

3.2. Pouch cells

As another demonstration of the effectiveness of the pinch–torsion test, comparison was performed on working Li-ion pouch cells from cell phones. The overall dimension of the cells was 90 mm × 55 mm × 4 mm with nine anode layers and nine cathode layers separated by polymer separators. These cells had a nominal discharge capacity of 2330 mA h and were charged to 4.1 V. During the tests, the axial displacement rate was fixed at 0.01 mm s^{-1} and rotation was introduced after the axial load reached 2200 N. The ISCr was determined by detecting a voltage drop of 0.1 V [2].

Loading curves from the pinch and pinch–torsion test are compared in Fig. 4, which overlapped each other until torsion was introduced in the latter (indicated by the circle in Fig. 4), where the pinch–torsion test curve started to deviate from the linear trend. This behavior was similar to that observed in Fig. 2. Both results indicated that axial penetration was eased by adding the torsion, i.e. less force was required for the same amount of axial deformation. This is likely because the torsion-induced shear force assisted the material flow in the lateral direction.

For these pouch cells, the torsional component decreased the failure load from approximately 3300 N to about 3100 N (Fig. 4). The reduction in the required axial load to induce ISCr was less prominent than that observed from the prototype cell study (Fig. 2). When the number of layers in a cell increases, the effective shear force on the internal layers may be decreased. In addition, the friction between the polymeric pouch material and the loading rods was different than that between the current collector materials (copper or aluminum), which could also affect the translation of shear force into the inner layers.

From post mortem examination, it was discovered separator ruptures (holes) typically occurred in the third or the fourth separator layer. The hole in the pinch–torsion tested cell had a smaller diameter (Fig. 5b) than that from the pinch-only test (Fig. 5), while the locations of the holes in both cases were in areas away from the center of the deformed zones.

3.3. Commercial cells

Comparison between pinch and pinch–torsion tests was further performed on some commercial Li-ion cells, which were used in a previous study [2]. These cells, labeled as “LIP C” in Ref. [2], have a nominal size of 4.5 mm × 42 mm × 61 mm with a capacity of 1500 mA h. Prior to testing, three LIP C cells were charged to 4.2 V. One cell was tested using the pinch test with an axial displacement rate of 0.01 mm s^{-1}. The other two were tested by the pinch–

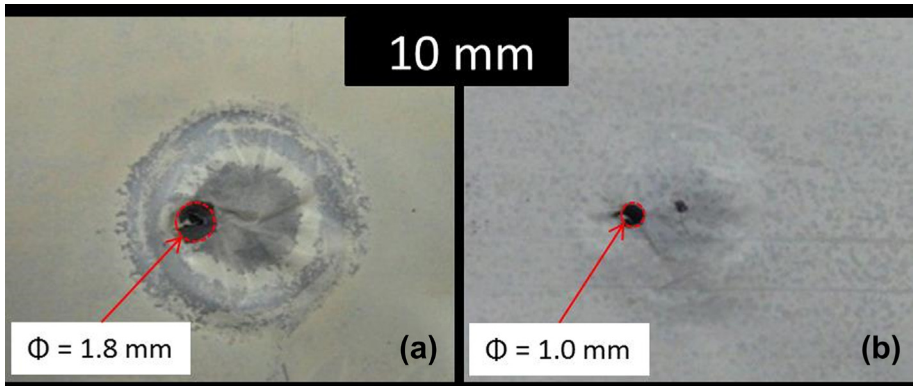

Fig. 5. Pictures showing the damaged separators after (a) pinch test, and (b) pinch–torsion test. Circle and arrows indicate holes in the separators.

torsion test using the same axial displacement rate. Rotation was introduced after the axial load reached 1780 N. The ISCr was determined by detecting a voltage drop of 0.1 V.

In the torsion test, ISCr occurred at an axial loading of 3274 N. After the load was removed, voltage continued to drop until the cell was completely discharged. Meanwhile, surface temperature was moderately increased. This result implied that the short spot was kept in contact after load removal. In contrast, the two cells tested under pinch–torsion experienced ISCr at axial loads of 3127 N and 3149 N, respectively. For both cells when the load was removed instant voltage recovery was observed without noticeable temperature rise.

Although pinch test seemed to induce larger damage to LIP C cells than pinch–torsion test, none of the three cells went thermal runaway. However, in the study performed by Cai and coworkers all LIP C cells charged to 4.2 V went thermal runaway [2]. This difference demonstrated the capability of the modified pinch–torsion test in distinguishing cell safety performance even at high SOCs.

Based on the above-mentioned results, it can be concluded that the pinch–torsion test is more effective than the pinch-only test when generating ISCr in Li-ion cells. Although the effectiveness of the torsional component tends to decrease as the cell thickness increases, the method has practical advantages since many modern battery designs involve large-thin Li-ion cells.

4. Pinch–torsion test of commercial Li-ion pouch cells

Using the new pinch–torsion test, two types of commercial Li-ion cells were tested. Both cells consisted of LCO cathodes and graphitic anodes. Type A cells had a nominal discharge capacity of 1150 mA h with a dimension of 66 mm × 35 mm × 5 mm, while Type B cells had a nominal discharge capacity of 2380 mA h with a dimension of 70 mm × 40 mm × 8 mm. These commercial cells were discharged using a constant current (0.5 A for Type A cells and 1.0 A for Type B cells) to 3.0 V. To charge a cell, a constant current step (0.5 A for Type A cells and 1.0 A for Type B cells) was first used until the target voltage was reached, followed by a constant voltage step until the current reached 5% of the rated 1 C current (57.5 mA for Type A cells and 119 mA for Type B cells). In addition to discharged/charged cells, a group of cells were tested in their as-received conditions for both Type A and Type B cells.

The charged voltage, discharge capacity, and the state of charge (SOC) for all Type A and Type B cells were summarized in Table 3. The SOC was calculated from the voltage profile. For all cells, the SOC reached 100% when using the above mentioned discharge/charge method; while the SOC of the as-received cells was approximately 46.9% for Type A cells and 60.7% for Type B cells. Since the as-received cells were at a “safe” condition per industrial practice for storage and shipping, their charge voltage and corresponding SOC were used as the lower limit in this study.

During the pinch–torsion test, the axial displacement rate was fixed at 0.01 mm s^{-1}. Rotation was introduced when the axial load reached 1780 N for cell A and 2890 N for cell B, which were approximately 50% of their respective loads to cause ISCr during

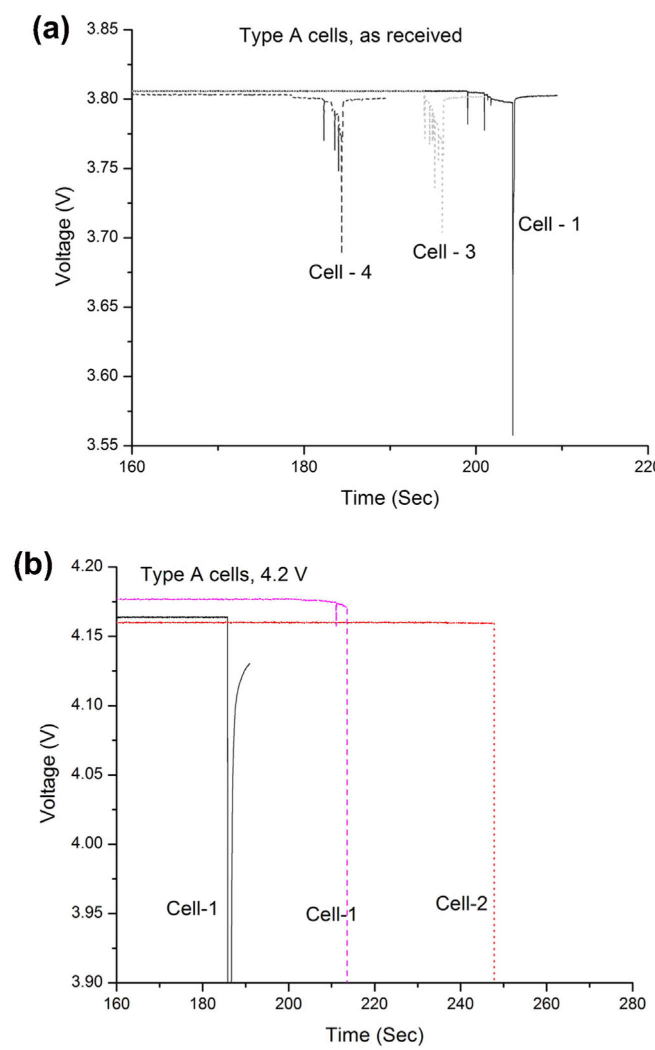

Fig. 6. Cell voltage of (a) as-received (3.8 V) and (b) fully charged (4.2 V) Type-A Li-ion cells near the end of pinch–torsion tests. Note: not all samples were shown to maintain the readability of the graph.

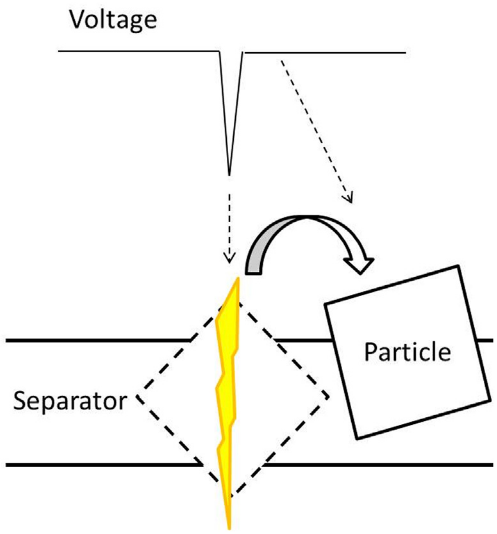

Fig. 7. Mechanism of the recoverable small voltage drop caused by electrode particle movement.

pinch-only tests. The open circuit voltage was monitored during the tests and the occurrence of ISCr was defined as a voltage drop of 0.1 V.

Loading curves when testing these commercial cells are similar to that shown in Fig. 4. For both cell types, the failure load does not seem to be a strong function of SOC (Table 3). However, the change of cell voltage toward the end of tests showed different behavior when SOC varied. For example, when testing the as-received (voltage ~3.8 V) Type A cells, the voltage curves were very "noisy" with multiple small drops and recoveries prior to ISCr (Fig. 6a). In contrast, when the cells were charged to 4.2 V, the voltage curves became much "smoother" near the end of tests – the final voltage drops appeared more sudden (Fig. 6b).

These "soft shorts" (voltage drops) were results of separator thinning and high resistance contacts between cathode and anode particles. During these tests, thinning of the separator progresses as the compression load increases. When the thickness of the separator is comparable to the size of the solid particles on the electrodes, these particles could penetrate the separator to create a microscopic local short leading to electrical discharge, which appeared as the small voltage drops in Fig. 6a. If the contact remains, the cell will continue to discharge at very small C-rate. Since the pinch–torsion test is a continuous deformation process, the particles could move away from the short spot and lose electrical contacts (voltage recovery) (Fig. 7). At 0.01 mm s^{-1} loading speed,

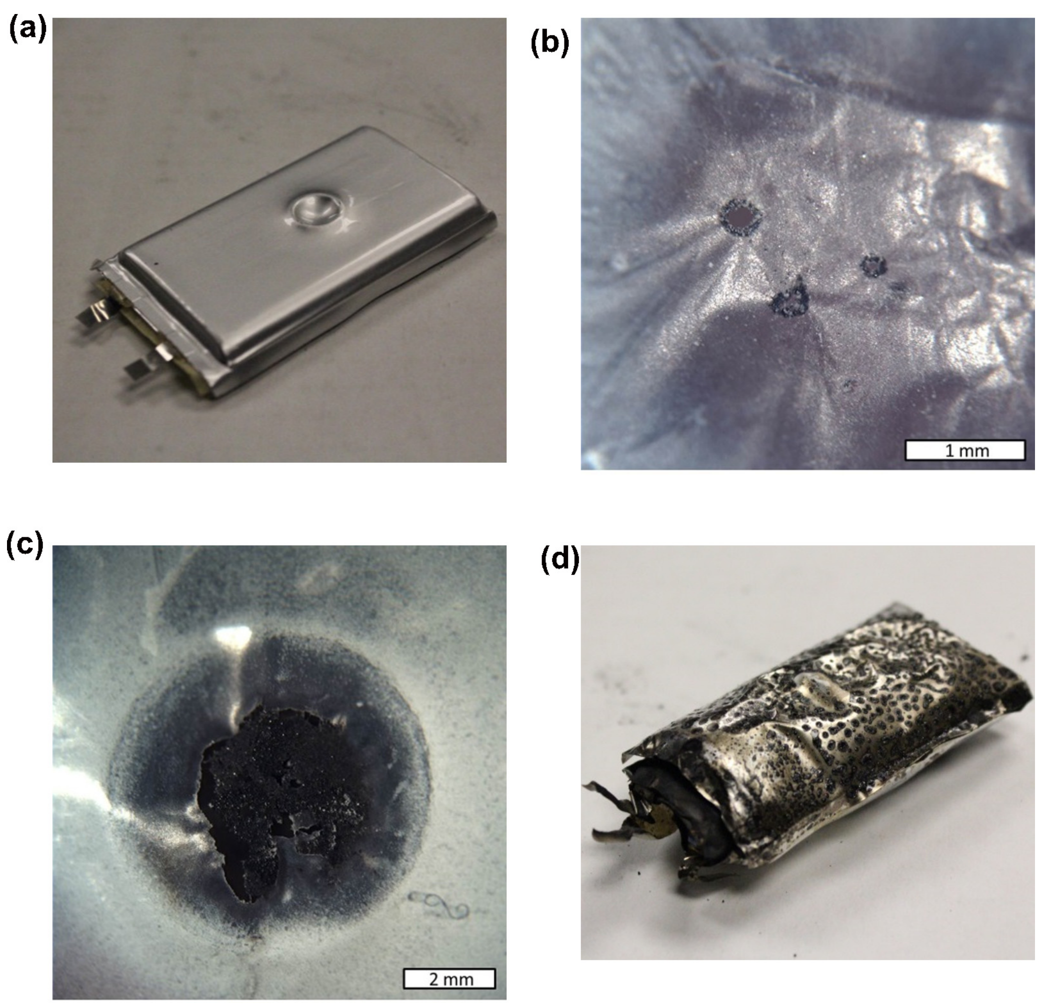

Fig. 8. Cell damage induced by the pinch–torsion test: (a) mechanical deformation, (b) submillimeter holes in the separator, (c) millimeter-sized holes with local melting of the separator, and (d) severe damage caused by thermal runaway.

Table 1
Thermal runaway risk (TRR) score for safety evaluation of Li-ion batteries subject to mechanical abuse testing.

TRR score	Damage description		Equivalent USABC hazard level (Table 2)
	Voltage	Temperature	
0	Soft short, small drops and recoveries	No significant temperature rise (<30 °C)	0–1
50	Continuous voltage drop without recovery	Significant temperature rise (30–100 °C)	2–3
100	Quick voltage drop	Rapid temperature rise (>100 °C within 2–10 s)	4–7

Table 2
Hazard levels defined in USABC [9].

Hazard level	USABC description
Level 0	No effect
Level 1	Reversible loss of function
Level 2	Irreversible defect/damage
Level 3	Leakage, mass loss <50%
Level 4	Venting, mass loss >50%
Level 5	Fire or flame
Level 6	Rupture
Level 7	Explosion

these "soft shorts" ($\Delta V = 3–10$ mV) were occurring in most cells. We set the test sensitivity of voltage drop at $\Delta V = 100$ mV; and a "return" motion of the loading rod was triggered once the 100 mV voltage drop had been detected. The key of successful ISCr tests is to set the voltage-drop sensitivity at the right level so the majority of cells will exhibit a typical "soft short" voltage drop and recovery response. As SOC increases with more energy to be released after the short circuit, the tendency of progressing into irreversible discharge (deeper voltage drops) and higher local temperatures will increase. Therefore, the occurrence of the small voltage drop followed by instantaneous recovery under load diminished as the cells were charged to higher voltages (Fig. 6b). For certain cells even after the removal of the load, the local temperature could rise above the onset of exothermic reactions and lead to thermal runaway.

Since multiple soft shorts appeared earlier during testing, it could be potentially used as a tool to study ISCr risks of separators and coatings on separator or electrodes. Since its effectiveness may be reduced when SOC increases it is advisable to keep SOC of such tests around 50%. On the other hand, lowering the voltage drop detection threshold could further increase the sensitivity of the ISCr tests. In the system used in the current study, it is possible to lower the limit from $\Delta V = 100$ mV to $\Delta V = 25–50$ mV. The exact testing protocols may be determined by organizations or groups setting test standards.

For both Type A and Type B, most cells only exhibited mechanical damage after testing (Fig. 8a) with no or limited temperature rise ($\Delta T < 10$ °C). Inside the cells, two different damage modes in the separator were seen: 1) submillimeter holes (~0.1 and 0.5 mm in diameter) (Fig. 8b), and 2) millimeter-sized holes with local melting of the separator (Fig. 8c). A few cells showed significant temperature increase after testing ($\Delta T > 30$ °C as measured on the surface). Some cells charged to 4.2 V went thermal runaway with massive venting, resulting in ruptured pouches and burned electrodes and separators (Fig. 8d).

Although there are some industrial methods for battery safety assessment, such as those suggested by USABC (Table 2) [9], they are more appropriate for battery systems rather than individual cells. A simple "pass or fail" criteria used by previous ISCr test methods is not an appropriate assessment and is probably the reason for limited adoption by the industry. Therefore, a thermal runaway risk (TRR) scoring system is developed without the use of post-mortem examination. The TRR score is only based on two continuously measured parameters: 1) cell voltage and 2) surface temperature. In the TRR system, i) TRR 0 is assigned when voltage drop is quickly recovered and the temperature rise is less than 30 °C; ii) TRR 50 corresponds to continuous drop in voltage, the final voltage drop is greater than the preset return voltage drop, and the temperature rise is between 30 °C and 100 °C; iii) TRR 100 indicates rapid voltage drop and fast temperature rise (within 2–

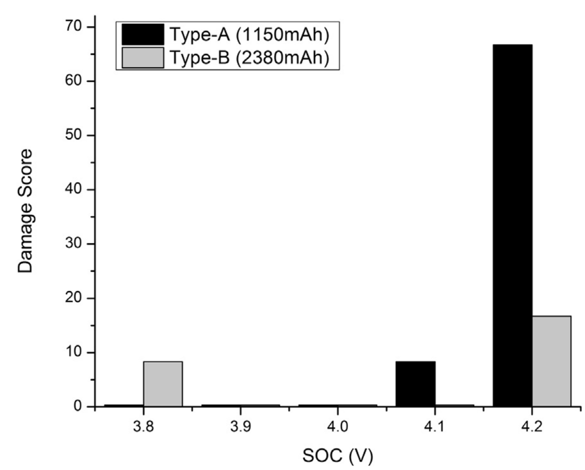

Fig. 9. TRR damage scores for Type-A and Type-B cells charged to various states. A voltage of 3.8 V is used for the as-received cells.

Table 3
Pinch–torsion test results of commercial Li-ion cells.

Cell type	Charge voltage (V)	Average discharge capacity (mA h)	SOC %	Number of test	Failure load (N)	Individual TRR score						Average TRR score
A	As received	540	46.9	6	−714 ± 19	0	0	0	0	0	0	0
	3.9	683	60.9	6	−771 ± 40	0	0	0	0	0	0	0
	4.0	873	76.5	6	−778 ± 31	0	0	0	0	0	0	0
	4.1	1000	95.6	6	−698 ± 32	0	0	0	50	0	0	8.3
	4.2	1125	100	6	−797 ± 64	0	100	0	100	100	100	66.7
B	As received	1500	60.7	6	−1217 ± 44	0	0	50	0	0	0	8.3
	3.9	1507	62.3	6	−1206 ± 27	0	0	0	0	0	0	0
	4.0	1925	76.9	6	−1183 ± 41	0	0	0	0	0	0	0
	4.1	2222	87.8	6	−1220 ± 48	0	0	0	0	0	0	0
	4.2	2503	100	6	−1157 ± 76	0	0	0	0	100	0	16.7

10 s) to greater than 100 °C. Comparison between TRR and USABC is given in Table 1.

Using the scale defined in Table 1, each tested cell was assigned a damage score and the average was calculated for each group (Table 3). For Type A cells, TRR score was low at low SOC (TRR = 0 when V ≤ 4.0 V) but rapidly increased to 66.7 when the cells were charged to 4.2 V (Fig. 9). In contrast, the variation of TRR score was very small (between 0 and 16.7) among different SOCs for Type B cells (Fig. 9). One of the as-received Type B cells received a TRR score of 50 (Table 3) due to noticeable temperature rise after testing. This was likely because the short spot remained in contact after the load was removed, which however is not typically seen at lower SOC. Since it is often desired to charge Li-ion cells to its maximum capacity, the TRR at high voltage needs special attention. It is apparent that Type B cells were less hazardous than Type A cells at higher SOC, although Type A cells behaved well at low voltages (≤4.0 V).

5. Conclusions

In this study, a modified pinch test was developed by introducing a torsion component. It has been experimentally demonstrated this pinch–torsion test can induce ISCr at a lower axial load with smaller ISCr spot size.

A thermal runaway risk (TRR) score method is also proposed to evaluate the thermal stability of cells during the pinch–torsion tests. As the hazard level increases, the corresponding TRR score increases. Testing results on two commercial Li-ion pouch cells were then evaluated and compared. It is shown that the combination of the pinch–torsion test and the TRR scores can distinguish the thermal stability of these Li-ion cells in the entire range of SOC, including the maximum charging voltage for these cells. Thus, it can be concluded that this method is a good candidate of safety evaluation for the battery industry.

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